

Magnetic order and superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$: a review

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Abstract

High- T_c copper oxides of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ family show a very clear case of *competition* between antiferromagnetic (AF) order and superconductivity. Magnetic order can, however, *coexist* with superconductivity, and the experimental evidence for frozen magnetic moments in superconducting samples is reviewed here. The primary characteristics of the magnetic order are summarized and some open questions are outlined, particularly concerning the intrinsic or extrinsic nature of this order around $x = 0.12$.

Key words: high- T_c superconductivity; magnetic order; stripes; magnetic resonance

1. Introduction

In 1988, R.B. Laughlin wrote about high T_c superconductors: "The systems in question are inherently magnetic. Stoichiometric La_2CuO_4 is an ordered spin-1/2 antiferromagnet and an insulator. Doping the material by substituting Sr for about 3% of the La destroys the magnetic order [...]. It is hard to understand how doping at this level could have destroyed all the spins. A more reasonable guess is that the extra holes make ordering more difficult, and that the spins are still present in some sort of 'quantum spin liquid' state" [1].

For a number of years thereafter, experimental studies failed to establish a consensus on whether localized spins indeed survived in metallic samples, possibly in a kind of spin-liquid state, or whether correlation effects in a metal were sufficient to explain the observed magnetic fluctuations. Despite much evidence that the superconducting phase retains some memory of the AF one [2], some considered that tangible signs of localized spins were lacking for superconducting concentrations ($0.06 \leq x \leq 0.28$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$): Néel order was rather far away ($x < 0.02$) and not much attention was paid to the frozen magnetic state for $0.02 < x < 0.06$.

Understanding of this issue has evolved since the discovery of charge stripes in $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$ [3] and related compounds [4]. In this class of materials, self-organization of the doped holes into linear ribbons leads to *long range magnetic order* in the hole-depleted regions, even for hole doping close to the optimal value for superconductivity ($\sim 15\%$). This spectacular "reappearance" of the spins was known before Tranquada's experiment, but the discovery of stripes renewed interest in magnetic order, and contributed to the view of high- T_c materials as doped antiferromagnets [5].

This paper is a short review on magnetic order in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductors. These represent a particularly interesting case, because they lie in between the LTT materials [4], where superconductivity is severely suppressed, and higher T_c systems such as YBCO where magnetic order is less obvious.

2. Reviewing literature

There are many reports of magnetic order coexisting with superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, starting with Kitazawa et al. in 1988 [6]. These results did not attract significant attention mostly because doubts were raised concerning the homogeneity of the samples, and because $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ was considered as an

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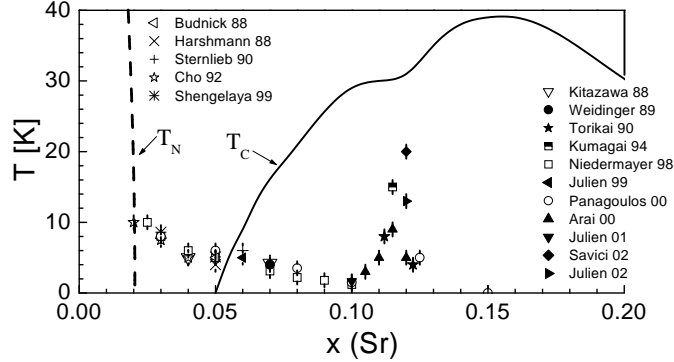


Fig. 1. Magnetic phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$: data points correspond to the temperature of magnetic freezing, T_g , inferred from μSR , NQR and NMR measurements (references are given in the bibliography). A systematic error $\Delta T_g = \pm 1$ K was chosen. Note that for Ref. [6] a concentration of $x = 0.07$ was used for the plot (0.08 in the original paper) since the sample has a T_c of 11 K. Other reports of a frozen magnetic state, or of strong slowing down of spin fluctuations, do not appear here. For example, Ohsugi et al. observed a broadening of the ^{139}La NQR lines due to the static internal magnetic field, but no freezing temperature was deduced [29]. Data from Fe EPR and Fe Mössbauer spectroscopy, which use a dilute impurity in the CuO_2 planes to probe the magnetic properties, are also omitted here (the role of impurities would require additional discussion). Other EPR data can be found in Refs. [30,31]. Data on marginal samples (anomalous T_c [32]) or with questionable criteria for T_g , or isolated experiments from a single technique [33] are not discussed. Another material that is omitted here is $\text{La}_2\text{CuO}_{4+\delta}$, which also shows superconductivity and magnetic order, but with some differences with respect to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

atypical member of the high- T_c family. This issue was reopened around 1998 [7,8,9] and most of the previous results were confirmed quantitatively.

Figure 1 shows most of the data available in the literature (to the author's knowledge), for the magnetic transition temperature T_g obtained from muon spin rotation (μSR), nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) in superconducting [6,7,8,10,11,12,13,14,15,16,17,18] and non-superconducting samples [19,20]. The reason for this selective presentation of the magnetic resonance data is twofold: numerous studies can be found in the literature which are lower-energy probes than neutron scattering (NS). Because the NS signal is quasi-elastic rather than purely elastic (the integration window is usually not less than 0.5 meV), and freezing of the moments is gradual in these compounds, the apparent onset of magnetic order occurs at higher T for NS than for magnetic resonance. NS studies of magnetic order in superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ can be found in Refs. [9,21,22,23,24,25,26,27]. On the other hand, magnetic resonance techniques can be considered as true low-energy probes: in the non-superconducting phase ($0.02 \leq x \leq 0.05$), the transition temperature T_g , defined at their time scale, is indeed very close (typically 1 K) to the T_g inferred from SQUID measurements [28], which are almost static.

3. Magnetic order in the phase diagram

The main features of the magnetic phase diagram on Fig. 1 can be summarized as follows:

- The agreement between the data is good, and there is no doubt that the magnetic phase for $0.02 \leq x \leq 0.05$ continues far into the superconducting region. Magnetic order thus coexists with superconductivity in underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.
- Except at the point where the T_c vs. x and the T_g vs. x lines cross, nowhere in the phase diagram does the magnetic transition coincide with the onset for superconductivity (see the discussion in [16] for the explanation of earlier confusion on this point).
- Magnetic order seems to persist at very low T for $x = 0.15$ [10,14,29], and up to $x = 0.19$ [34], although there is not full agreement on this issue [35].
- Some scatter in the data can be seen around $x = 0.12$. For example, a μSR study detects the appearance of frozen moments near 20 K in $\text{La}_{1.88}\text{Sr}_{0.12}\text{CuO}_4$ [17], while an NMR study in a very similar single crystal, defines $T_g = 13$ K as the T at which the *average* relaxation rate $1/T_1$ is maximum [18]. If the volume fraction of magnetic order grows on cooling down (distribution of T_g values), the discrepancy between the criteria is not surprising. In addition, the strong x dependence of T_g around $x = 0.12$ may contribute to the scatter between data from different samples, and the somewhat higher energy scale of μSR with respect to NMR may become noticeable since T_g is higher.
- In any event, there is a clear *enhancement* of T_g around $x = 0.12$, coinciding with a slight suppression of T_c . This suggests the same '1/8 anomaly' as in LTT species, although with the following differences: Superconductivity is only weakly affected here (note however that a few $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples around $x = 0.12$ have an anomalously low T_c , which is yet to be understood [23,32,36]). The maximum of T_g seems to be oc-

cur around $x = 0.115$ - 0.12 rather than at $0.125 = 1/8$.

- The overall magnetic phase diagram in Fig. 1 is similar to that of LTT $\text{La}_{1.8-x}\text{Eu}_{0.2}\text{Sr}_x\text{CuO}_4$ [37], but the peak of T_g around $x = 0.12$ is much narrower in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. This makes a clearer distinction between the behavior close to $x = 0.12$, and the monotonic decrease of T_g *vs.* x for $x \leq 0.10$.

4. Other features of magnetic order

- For $0.02 \leq x \leq 0.05$, characteristic features of spin-glasses (in the loose sense: these features are also seen in diluted antiferromagnets) are observed in the bulk magnetization [28]. Because of the Meissner effect, no such study could be performed in superconducting samples. However, the continuous decrease of T_g from $x = 0.02$ up to $x = 0.10$ suggests that the magnetic state is similar on both sides of the non-superconductor to superconductor transition. Furthermore, μSR [7,10,14] and NMR [8,16,38] show that sizeable disorder (spatial inhomogeneity) in both the spin dynamics and the static local magnetization also exists for $x \geq 0.06$. The slowing down of magnetic fluctuations is also similar above and below $x = 0.06$, and is more gradual than for a conventional 3D Néel transition. Magnetic order is thus considered to have some glassy character in superconducting samples, and the transition temperature is usually called T_g .

- The frozen magnetic state between $x = 0.02$ and $x = 0.10$ has been named a 'cluster spin-glass', in order to reconcile the glassy features with the existence of domains of staggered magnetization [8,20,39]. It has also been clear that some kind of charge segregation/order is necessary in order to explain the existence of frozen AF clusters at concentrations as high as $\sim 12\%$. However, it was recently shown that the frozen state could actually be described as diagonal (with respect to Cu-O bonds) stripes for $x \leq 0.05$ [24], within the neutron scattering time window, collinear stripes for $x \geq 0.06$ [9,21,22], and the coexistence of both around $x = 0.06$ [26]. The existence of magnetic stripes explains the AF domains of the cluster spin-glass, but it does not allow one to deduce whether all of the spatial inhomogeneity is due to the stripe pattern or whether additional phenomena, such as phase separation between striped and non-striped regions, take place.

- The magnetic order in question is not magnetic-field induced. Lake et al. observe an enhancement of the Bragg peak intensity by applying a field, and a change in its T dependence, but magnetic order at $x = 0.10$ is known to exist even in zero field both from measurements by the same authors [27], and from earlier studies [7,14,16,21,29] (see also [23] for $x = 0.12$). Note that the T at which a neutron diffraction signal ap-

pears does not seem to vary with the field [27], and that no strong modification of slowing-down with the field could be detected in NMR [8,16].

- The magnetic correlation length at low T is shortest around $x = 0.06$ ($\xi \sim 20$ Å) and has a strong peak around $x = 0.12$ ($\xi \geq 200$ Å) [25,26], where stripes are actually slanted [22]. The ordered moment decreases with x up to $x \simeq 0.10$ but it seems to be enhanced at $x = 0.12$ [7,13,17,25].

5. Is magnetic order intrinsic ?

A recent μSR study for $x = 0.12$ indicates that the frozen magnetic regions represent not more than 18 % of the sample volume, at low T [17]. This immediately raises the question of the intrinsic character of the magnetic phase [40].

Savici et al. propose that there is phase separation between regions with (striped) magnetic order and superconducting regions without magnetic order [17]. Alternative and/or complementary explanations should however be considered. First, there is evidence that local LTT distortions exist in the LTO phase [4] of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [41,42,43]. As noted in Refs. [41,44], this should cause local pinning of stripes, and thus nucleate magnetic order. The fact that T_c is only weakly affected in $\text{La}_{1.88}\text{Sr}_{0.12}\text{CuO}_4$ and the absence of a $1/8$ -anomaly for T_g in a Y-doped $\text{Bi}2212$ [34], a material which does not show the LTT instability, could support this hypothesis. Another possibility is that the magnetic fraction at the μSR time scale is reduced by rapid spin flips. These spin flips might be produced by transverse stripe fluctuations [47]. It is instructive to remark that in LTT species, where stripes are supposedly more static, there is already evidence for substantial averaging of the local magnetization at the NMR time scale [45]; a magnetic volume fraction of 100% is observed at $x = 0.12$, but it is reduced by *half* at $x = 0.15$ [46]. At present it is thus unclear whether the T_g anomaly and the reduced magnetic fraction in μSR for $x = 1/8$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ are intrinsic or if they are related to extra pinning by lattice distortions in some parts of the sample.

For $0.02 < x \leq 0.10$, magnetic order seems to be intrinsic as a large fraction, if not all, of the muons see an internal field, according to Refs. [6,7,10,12].

All studies to date and the good agreement between data sets from many different samples, point to the existence of bulk superconductivity in these systems, except close to the onset value $x \simeq 0.06$ and possibly at $x = 0.12$ (this case is not clear) [7,12,17,48]. Note that these studies ascertain that the samples studied by NMR or μSR are representative of superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, but they do not rule out the existence

of normal regions and/or unpaired carriers.

In conclusion, coexistence of magnetic order with superconductivity is intrinsic in a significant part of the phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Since these are bulk phases, without any hint of macroscopic phase separation, the coexistence has to occur on a small length scale. Nevertheless, the data discussed here do not seem to provide firm answers to crucial questions [49]: Is the stripe picture able to account alone for the coexistence? Is there a strong hybridization between the magnetic and the superconducting entities or should they be considered as distinct phases? More generally, which ingredients make the coexistence possible: spatial segregation, different orbitals (Cu and O), different energy scales, etc.?

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